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Translated by the Chair
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The principal task of the Fyodorov's Crystallochemical Analysis is known to be the determination of substance after the outer form of the crystal.

E.S.Fyodorov thought it possible, while bringing about such a determination, to reveal by the way the scheme of the crystalline structure (lattice type) also by investigating the outer form of the crystal.

Because of the recent development of the X-ray structural analysis this tentative is generally recognized as belonging to the past of science.

It will be seen later that this opinion is not quite justified. Though it does not contribute to the deciphering of structures, Fyodorov's technique may be of use even nowadays, if applied to the stricter delimitation of some crystallogenetic problems which are of interest from the mineralogical and geochemical point of view. However, up to now the Crystallochemical Analysis has been intended exclusively for the determination of substance after its crystalline forms. It is that trend of Fyodorov's theory that was mostly paid attention to and followed by his disciples and successors, who have later on created some simplified modifications of the analysis in question (methods elaborated by A.K.Boldyrev and T.V.Barker).

Such an approach to the development of the Crystallochemical Analysis is particularly pronounced in the well-known article by A.K.Boldyrev "Principles of a New Method of Crystallographical Substance Diagnosis"

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According to Boldyrev, "the only absolutely necessary basis for the diagnosis of crystals consists in the empirical data concerning their goniometry and the Law of Constancy of Angle". The main principle of Boldyrev's method is the direct transition from the measurement of a crystal to the determination of its substance. The determination of the structural pattern and the definite orientation of the crystal (according to Fyodorov) are omitted.

Here is the scheme of the analytical procedure as it was proposed both by Fyodorov and by Boldyrev:

Fyodorov's procedure

I. Measurement of angles; 2. Definite orientation of the crystal; 3. Structure determination; 4. Substance diagnosis.

Boldyrev's procedure

I. Measurement of angles; 2. Substance diagnosis.

Due to the recent publication of the works by J.D.H. Donnay, and J.Melon, P.Terpstra, J.H.Haan, M.Porter and E.Spiller as well as of the Soviet "Crystal Determination Guide" the problem of substance determination after the angles between faces may be considered as thoroughly investigated. A further advance in this respect may be expected only from compiling supplementary volumes to determination guides and perfecting some details of goniometric technique.

However, the possibilities offered by the crystalline form are not limited to the determination of substance after angles. More than thirty years ago A.V.Shubnikov and O.M.Shubnikova wrote on this subject: "Examining the infinite variety of quartz crystal forms, Ste-

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no found out a property common to all of them: the angles between corresponding faces have a constant value.

Though this discovery by no means implies that the outer form of crystals is not controlled by any other laws, scientific crystallography in its subsequent development thoroughly ignored such laws... Any further studies of the subject must necessarily be based upon the empirically established fact that the form of a crystal is not only a function of its structure but also that of the medium it grows out".(A.V. Shubnikov and O.M.Shubnikova, 1926).

A conclusion ensues that by investigating the form of a crystal it is possible to determine not only the substance but also the physico-chemical properties of the medium as well as its spatial geometrical features.

To solve such crystallogenetic problems it is necessary to examine, on one hand, various forms of crystals of the same substance originating in various media (as to minerals,in various deposits) and, on the other hand, the deviations of the real crystalline forms from the ideal ones.

To establish the physico-chemical characteris - tics of the medium forming a crystal after the configuration of the latter it is necessary to take into account the enormous amount of the available empiri - cal data accumulated during more than two centuries' work of crystallographers and mineralogists.

These data are summarized in the well-known works by P.Groth, V.Goldschmidt, C.Hintze, J.Dana,

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P.Niggli and others. It is obvious that, unlike the existing crystal determination guides, the future Crystallogenetic determination guide will not deal solely with some ideal polyhedron obtained from statistical data concerning a number of crystals of the same substance (that was the way followed by E.S.Fyodorov and T.V.Barker in compiling their tables). It will necessarily take into account various habit forms of a given substance as well as physico-chemical characteristics of the conditions governing their genesis.

This approach is the only one permitting the use of crystalline forms as physico-chemical indicators of the medium.

It is noteworthy that Boldyrev's "Crystal Determination Guide" is a step forward as compared with other guides. A number of drawings representing crystals of the same substance with various forms are inserted in this guide. Should the drawings be followed by the data on the matrix generating these crystals (for minerals, by the references to the enclosing rocks, at least), a kind of Crystallogenetic Determination Guide would be at hand, though it would be an imperfect one. Theoretical reasoning may also be of use for this purpose.

Many authors mentioned the variability of the outer form of crystals depending on the dynamic behaviour of structures under various physico-chemical conditions. A classical example of this behaviour is furnished by the crystals NaCl (A.Wells). Let us recall what it consists in. In a neutral medium the atoms Na and Cl in the rock-salt structure become, so to say,

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"equal-righted"(which means that little spheres representing the sodium and chlorine ions in the model of the structure are to be coloured uniformly. Under such conditions the structure is analogous to a simple cubic lattice the densest nets of which correspond to the faces of the cube.

That is why, according to Bravais's law, crystals of salt settled out of neutral aqueous medium have cubic forms. In acid or alkaline media only ions of one kind acquire the dominating significance (either Na or Cl). In this case the structure NaCl is represented as a face-centred cubic space lattice (in the ordinary model of the structure NaCl atoms of one colour get forward and those of the other fade away)(fig.I). Octahedron faces are known to possess the densest nets in the face-centred cubic space lattice. It is with this phenomenon that the octahedral form of sodium chloride crystals grown out of active (not neutral) solution is connected. Consequently the variability of a crystal form due to the dynamics of structure in media of different chemical characteristics gives us the idea about the chemical properties of any particular medium.

Let us take for another example the crystals of fluorite (fig.2). For this mineral, in case of active media, it should be expected the appearance of either cubic crystals (in the model of CaF_2 ions of fluorine get forward, and those of calcium fade away, thus creating an ordinary cubic lattice), or octahedral crystals (ions of calcium get forward forming a kind of a face-cubic lattice). At last rhombo-dodecahedral forms will

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appear in neutral media (in the structure of CaF_2 with "equal righted" ions of Ca and F (110) are the densest nets).

All these varieties of crystals are known well enough. J.Dana describing in his "System of Mineralogy" the forms of fluorite emphasizes that the ordinary crystals are usually cubic and in rather rare cases octahedral. Quite recently V.F.Barabanov has shown by special examples the definite sequence of change of fluorite habit forms, i.e. octahedron - rhombo-dodecahedron-cube. This evolution is due to the subsequent decrease of concentration of the solution forming the mineral and to the alteration of the corellation in the medium between Ca and F.

We dwelled on this question narrowly to show the importance of using in some cases Fyodorov's approach to the definition of the "lattice" type after the outer form of a crystal.

In fact with an active medium putting forward in a complicated structure the significance of ions of one kind, Fyodorov's method enables us to determine in the simplest cases the type of a space lattice formed by these ions.

In case of neutral medium, when the aggregate of atoms of a structure forms a kind of one total space lattice in which heterogeneous atoms are supposed to be homogeneous, Fyodorov's method once more gives the idea about the location of all atoms forming the structure. It goes without saying that the modern approach to this problem must introduce essential cor-

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rections into Fyodorov's technique. The latter may be applied only to the crystals of homogeneous origin(i.e. to the crystals of the deposits of the same type) and helps us to understand rather the behaviour of a crystal structure in different media than the structure itself.

Unfortunately the data obtained in the course of experimental work based on the above principle are still rather scarce. Much work is required to use it properly in creating the Crystallogenetic Determination Guide.

It should be borne in mind that this method allows to solve in the most generalized way the task of determining the chemical characteristics of the medium after the outer form of the crystal by studying the dynamic behaviour of its structure.

Concerning the problem of the definition of the medium characteristics it is important to emphasize the necessity of examining material with complicated crystallographic forms viz. skeletal formations, induction surfaces, forms of solution, pyramids of growth, composite crystals and twins considered from the point of their general form, etc.

At present we have completely elaborated the general theory of the crystal forms covering the complicated forms as well. It is convenient for the description of the latter to use peak, edge, and face forms represented by bundles and polyhedrons with re-entrant angles.

The deduction of these forms is now completed.

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There exist 9 flat peak forms (i.e.peaks connected by elements of symmetry) (fig.3.4). Thickenings at the ends of snow-flake rays may give an idea of such formations). The number of spatial peak forms is 47 (fig.5). The number of flat edge forms (i.e.edges connected by elements of symmetry) is 27. (They are very convenient for the description of microcrystalline specimens) (fig.6).

The number of edge bundles (edges connected by elements of symmetry and converging in one point) is 47. (fig.8).

The deduction of carcass edge forms, coinciding with the surface of the crystal polyhedron was carried out by V.I.Mikheyev, I.I.Shafranovsky and S.Sh.Guendelev.

The number of carcass edge forms for crystals of lower syngonies is 18, for tetragonal crystals it is 52, for hexagonal and trigonal syngonies - 90, and for cubic crystals - 143 (the total is 303).

These forms are particularly convenient for exact description of the striae on the faces (fig.9).

The deduction of simple face forms as bundles and polyhedrous with re-entrant angles is of particular interest.

All the cross-sections for crystallographic prisms, the common ones as well as the ones with re-entrant angles, are to be seen in fig.10.

Fig.11 represents eight geometrical varieties of a cube. Positive (filled with some substance) as well as negative (hollow) ones are among them.

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From the point of view of geometry skeletal formations as well as twinning crystals often correspond to such forms.

For instance the twin of two intergrown tetrahedrons (tetrahedrite) corresponds to one of geometrical varieties of octahedron with re-entrant angles (fig.12).

Complicated forms of crystals are often good indicators of crystal environment, pointing to its viscosity, the presence of impurities, etc.

It is obvious that the solution of crystallogenetic problems should be based upon these forms.

Now we shall proceed to the definition of spatial geometrical peculiarities of the environment on the base of real (not idealized) crystal forms.

It is well known that ideally formed crystal polyhedrons are to be found in nature and in laboratories only as rare exeptions. As a rule we have to deal with distorted forms. These distortions, however, follow certain regularities connected with the conditions of crystal formation.

They depend mainly upon the symmetry of the crystal environment (P.Curie, A.Shubnikov, G.Lemmlein). Hence the distored forms must be taken into consideration for the solution of crystallogenetic problems. Here we are helped by the general theory of the outward (apparent, pseudo) symmetry of distorted forms and crystallographyc pseudo-forms which are components of a crystal.

A simple pseudo-form is a part of a real simple form and corresponds to the sum of faces connected

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by elements of outward (pseudo) symmetry of a polyhedral crystal.

As an example we can cite a quartz crystal with outward symmetry "p" (one pseudo-plane of symmetry, fig. 15). The front faces of its hexagonal prism disintegrate into a "pseudo-dihedron" (d) and a "pseudo-monohedron" (m). The front rhombohedron faces form a "pseudo-monohedron" (m') and a "pseudo-dihedron" (d') too.

It is easy to determine according to characteristic striae and adjoining formations that (d) and (m) belong to one hexagonal prism, whereas (d') and (m') belong to the rhombohedrons. But in order to determine the symmetries of crystal environment it is useful to take into account the presence of pseudo-dihedrons and pseudo-monohedrons.

From the foregoing it is clear that nearly all the combinations of faces on real (not idealized) crystal polyhedrons, can be subdivided into simple pseudo-forms.

The main reason for the formation of pseudo-forms is believed the symmetry of the environment (the crystal forming medium). In addition to this it should be mentioned that the external symmetry of real crystal units preserves only those elements of the true crystal symmetry which are identical with the like elements of the environment symmetry.

It is seen from the above discussion that for determining the symmetry of the crystal forming medium the description of a real individual crystal is to contain the data on its external symmetry together with the indication of all the simple pseudo-forms observed on it.

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At present there are tables compiled to demon - strate what cases of the environment symmetry any external symmetry of the crystal correspond to and what pseudo-forms are apt to form on it.

Table I given in this paper represents data for the simplest cases of the environment symmetry (fig. I4, I5).

In all the cases represented the environment may be liquid, gaseous or polycrystalline granular but it is to be statistically homogenous (Such cases are discussed in details in my book viz."The Crystals of Minerals" by Shafranovsky (1957). The environment symmetry is everywhere presented as a group of points i.e. a totality of the symmetry elements crossing in one point which is the centre of the crystal.

The formation of definite individual simple pseudo-forms characteristic of a certain pseudo-symmetry (see table I) corresponds to all the simple cases mentioned.

When considering the crystal of any definite symmetry, the number of such pseudo-forms greatly diminishes.

To make the crystallogenetic deductions precise it is advisable to bear in mind the sculptures of growth on the faces as well as all the crystallomorphological features involved

From the foregoing it follows that there is a definite basis for compiling a Crystallogenetic Determination Guide which appears to result from the further development of the Fyodorov's Crystallochemical analysis.

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The aim of the former crystal determination guides was the definition of substance after the forms of polyhedrons.

The new Guide will inform about the physico-chemical and geometrical properties of the environment also on the basis of the outer form of the crystal.

The Crystallogenetic Determination Guide is supposed to consist of two parts. The first, introductory part will contain tables concerning either all the crystals in general or groups of crystals belonging to various syngonies and cathegories. Table I is an example of these tables. The second special part is to contain data on particular crystalline substances. Here will be given the results of the crystal structure analysis of a particular substance pertaining to the possible appearance of any faces, the data on diverse crystal habits observed in crystal genesis under different conditions, the tables with a list of composite forms and pseudo-forms possible for the crystals of the corresponding kind of symmetry, etc.

Of course, the Crystallogenetic Determination Guide may be of use only after defining the crystal substance. That is why such a guide is to be considered as a special volume supplementary to those available.

The compilation of the Crystallogenetic Determination Guide will require much work on collecting and systematizing material as well as close critical revision of existing publications. Such a work not

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to be attempted by one scientist is to be carried out only by joint efforts of crystallographers, mineralogists and chemists.

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Tabl.I

Environment symmetry	External crystal symmetry	Ideal crystal forms	Pseudo-forms
$C\infty L_\infty \infty P$	The totality of elements of the ideal crystal symmetry	All real forms	-
$L_\infty \infty P$ (Fig.Ih)	Ln ⫶ P (Ln.P.-)	Di-n-gonal and n-gonal pyramids and prisms, orthorhombic pyramids and prisms, domes pinacoids, pedions	Di-n-gonal and n-gonal pyramids and prisms, ortharhombic pyramids and prisms, domes, pinacoids, pedions.
P (fig.I5)	P (-)	Domes, pinacoids, pedions	Domes, pinacoids, pedions.
-	-	Pedions	Pedions

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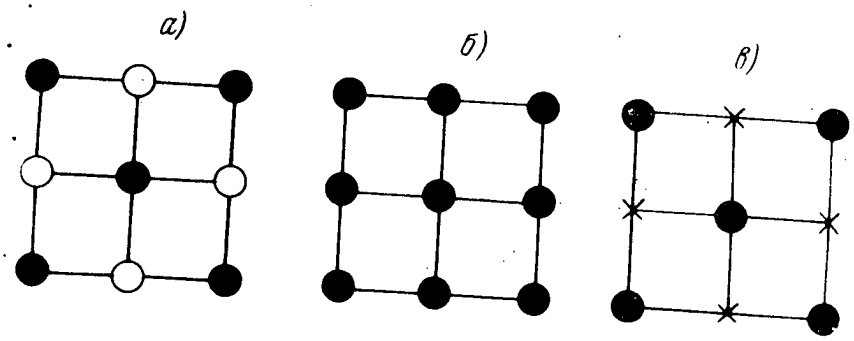

Fig 1

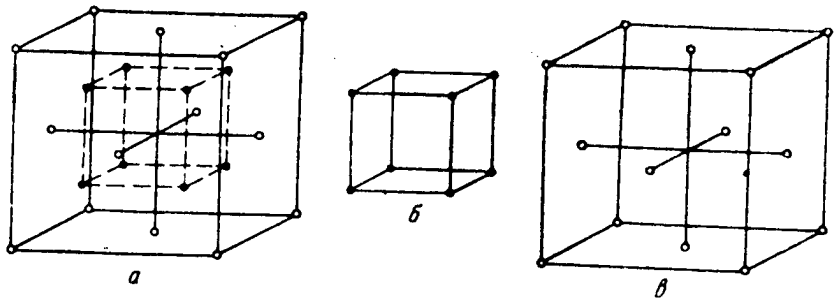

Fig. 2

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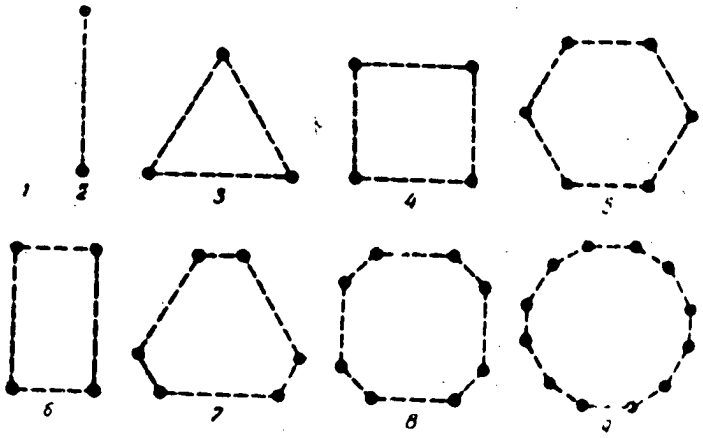

Fig 3

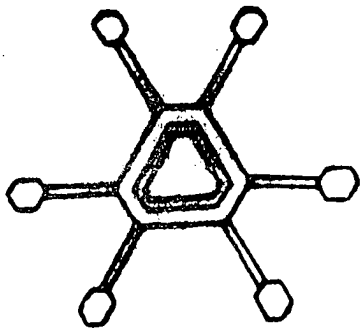

Fig 4

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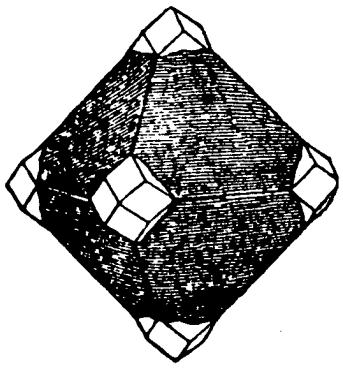

Fig 5

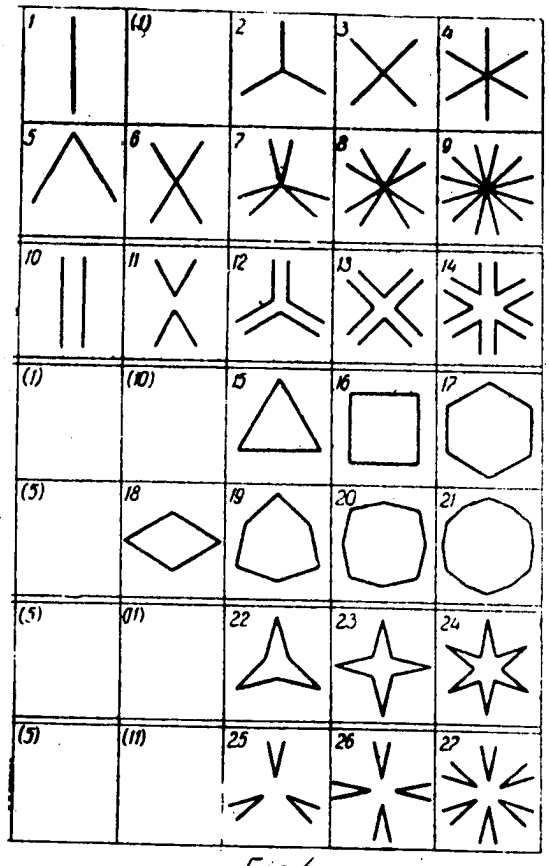

Fig 6

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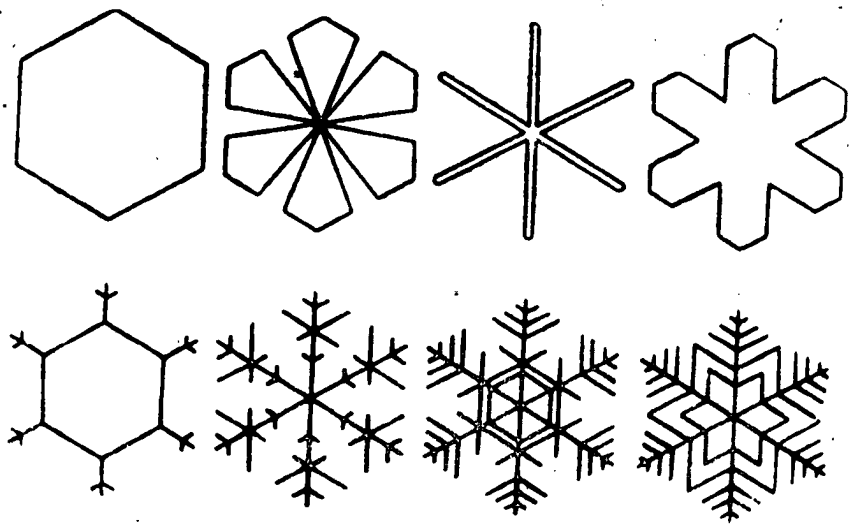

Fig 7

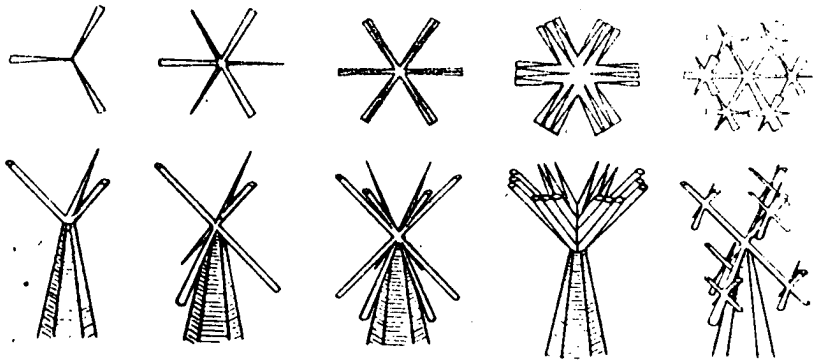

Fig 8

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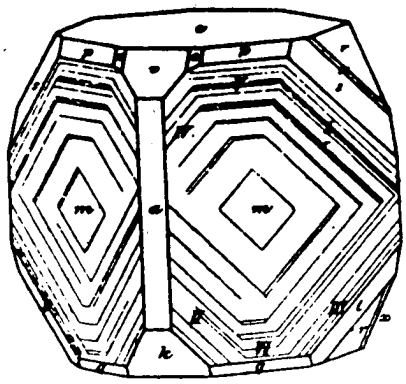

Fig 9

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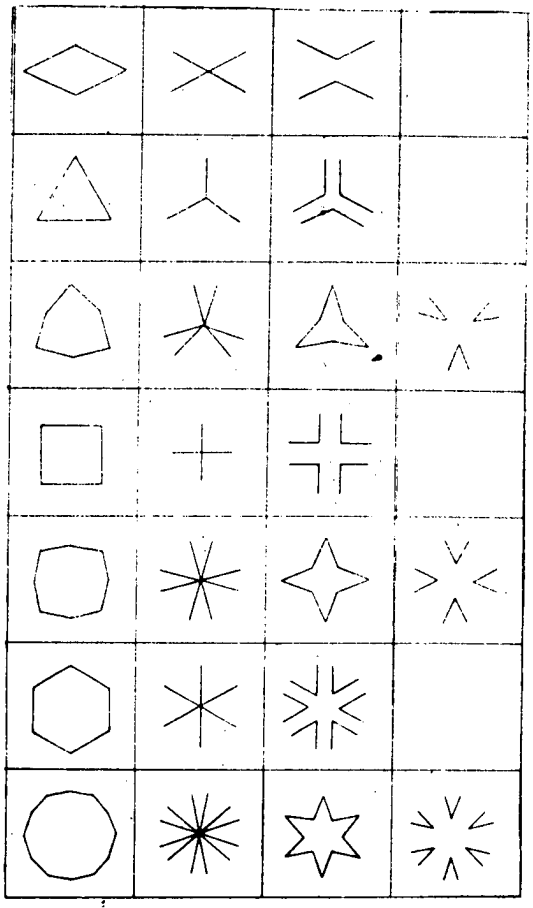

Fig. 10

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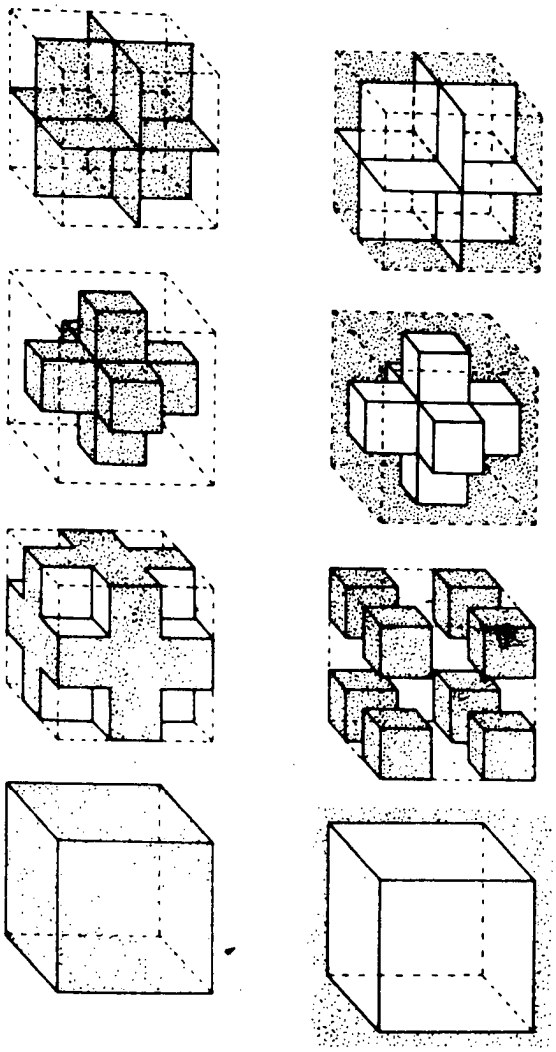

Fig. 11

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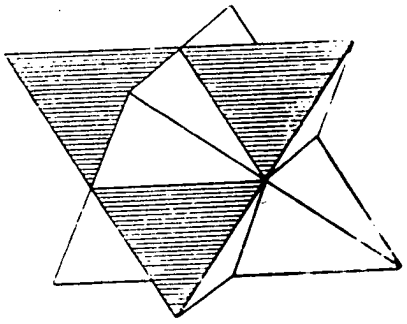

Fig 12

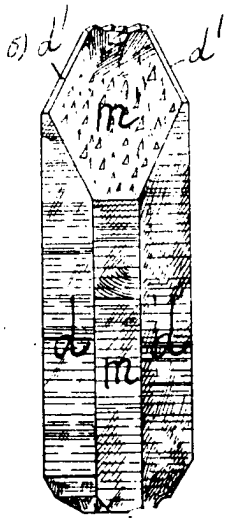

Fig 13

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$$R = \frac{\Sigma |F_i - F_j|}{\Sigma |F_i|} =$$

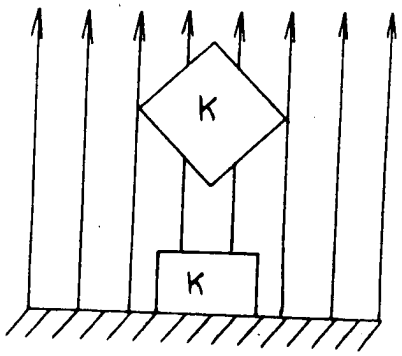

Fig. 14

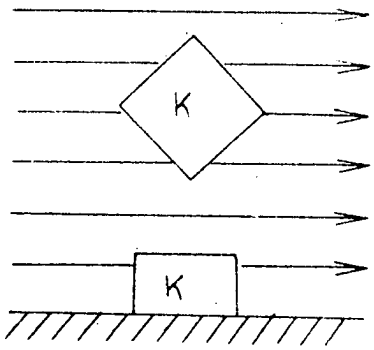

Fig. 15

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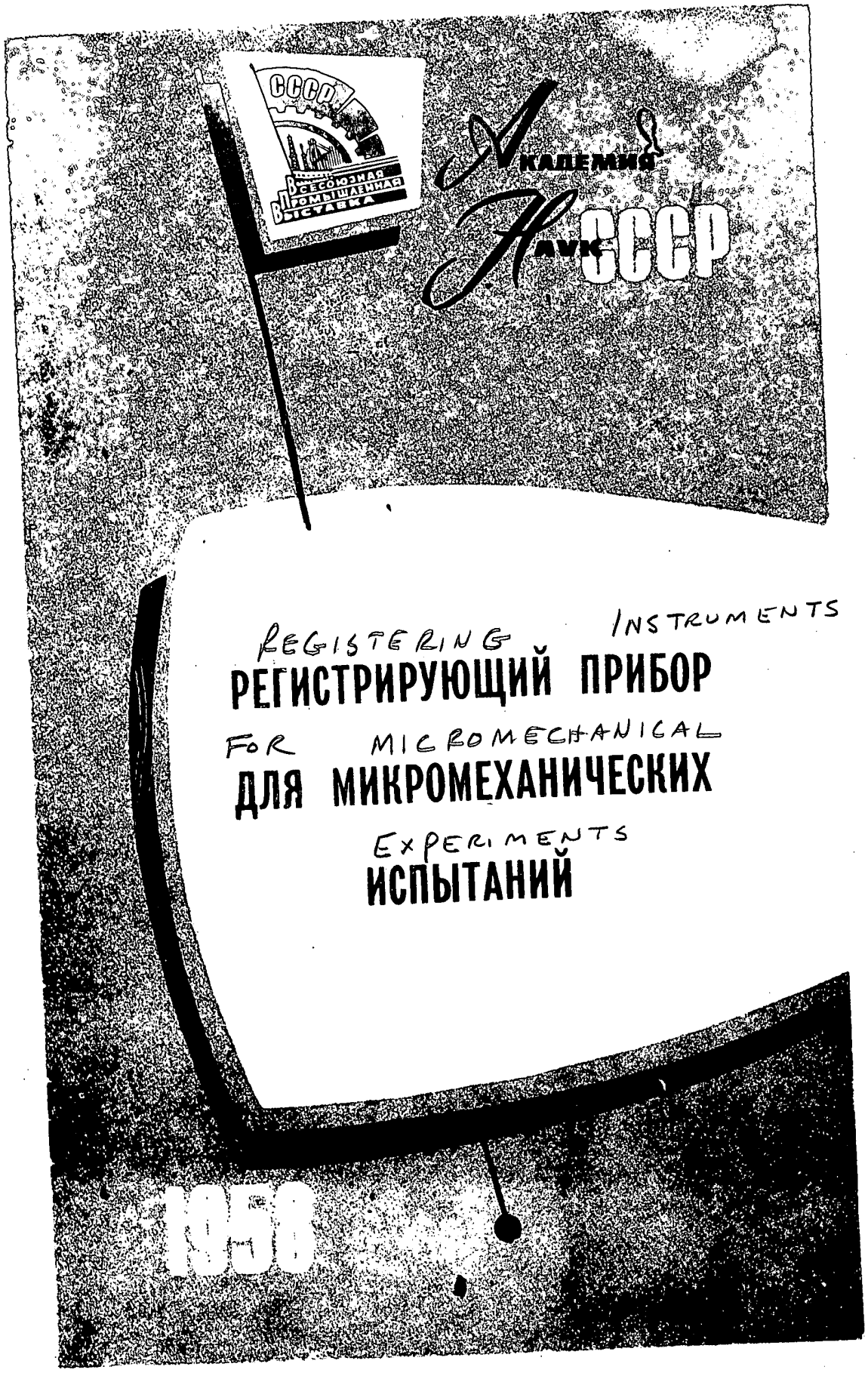

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Прибор предназначен для автоматической записи кривых сжатия, растяжения и релаксации механических напряжений малогабаритных образцов. Минимальные размеры образцов на сжатие: высота 3 мм; диаметр 2 мм. Прибор позволяет производить испытания при различных скоростях нагружения (разгружения) и температурах.

Напряжения, действующие на образец, измеряются жестким фотоэлектрооптическим динамометром. Принцип действия динамометра основан на использовании явления фотоупругости. Измерителем служит стеклянный параллелепипед. Сила, действующая на этот параллелепипед, определяется путем измерения в нем оптической разности хода, обусловленной аномальным двупреломлением. Разность хода измеряется фотоэлектрическим методом: при помощи фотоэлемента регистрируется интенсивность света, прошедшего через скрещенные поляроиды и помещенный между ними стеклянный параллелепипед.

Электрооптическая схема динамометра изображена на рис. 1.

Пучок света от лампы накаливания 1 (2,5 в; 0,8 а) проходит через конденсатор 2 и попадает на наклонную стеклянную пластинку 4. Часть света, прошедшая через пластинку 4, направляется через поляризатор 5, стеклянный измеритель 7, анализатор 8, скрещенный с поляризатором 5, и попадает на измерительный фотоэлемент 9. Часть света, отразившаяся от пластинки 4, проходит оптический клин 10 и попадает на компенсационный фотоэлемент 11. Кроме этих деталей, оптическая система включает

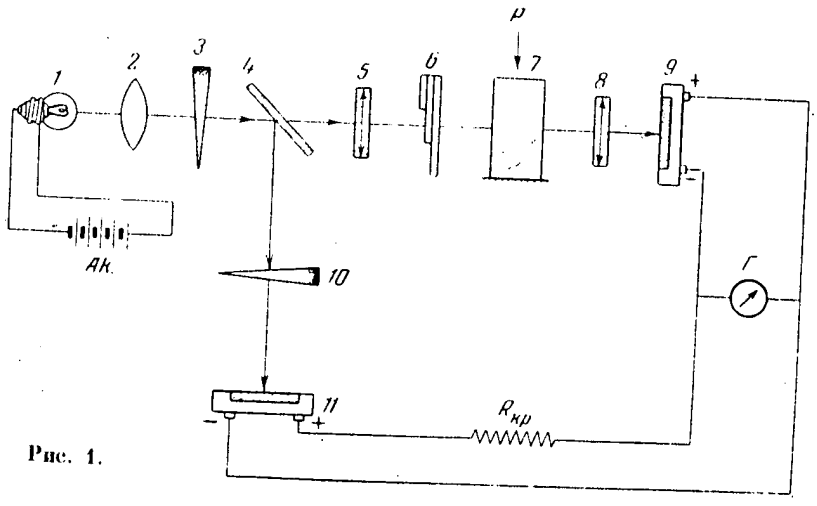

Рис. 1.

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в себя пластинки дополнительной разности хода 6 и оптический спектрально нейтральный клин 3. Дополнительная разность хода 6 необходима для создания приблизительно линейной зависимости интенсивности света, прошедшего систему, от разности хода. Оптический клин 3, поглощая часть света, позволяет изменять чувствительность системы. Компенсационная часть системы, которая состоит из оптического клина 10 и фотоэлемента 11, включенного навстречу измерительному фотоэлементу 9, служит для точной установки электрического нуля динамометра. Запись фототоков производится фотографическим способом. Для записи фототоков могут быть использованы различные заводские самописцы: типа пирометра Курнакова, ЭПП-09, ПС-383, МФ-4 и др. При длительных испытаниях на релаксацию, измерения ведутся визуально. Для демонстрации на Выставке прибор снабжен специальным регистрирующим устройством.

Тарировка прибора, т. е. определение зависимости отклонения луча записывающего устройства или отсчета по шкале гальванометра от силы, приложенной к измерителю 7, осуществляется при помощи рычажного нагрузочного приспособления.

Конструкция деформирующего устройства дает возможность вести нагружение испытуемого образца с постоянной скоростью. При помощи коробки скоростей и смены моторов можно изменять скорость вертикального движения деформирующего винта (т. е. скорость деформации) от $8 \cdot 10^{-7}$ до 10^{-1} мм/сек (в 125 000 раз). В этих пределах можно устанавливать 25 различных скоростей. Для испытаний при различных температурах применяются терморегулируемые устройства. В интервале от -70 до $+200°$ С используется ультратермостат; для получения более высоких температур (до 600° С) применяется электронагреватель. Регулирование температуры с точностью до $\pm 0{,}5°$ С производится в этом случае при помощи электронного регулятора ЭРМ-47 от термопары. Наружные части деформирующей системы (столбы и фланцы), изменение температуры которых может вносить искажения в измерения, защищены водяными рубашками. В этих рубашках циркулирует вода комнатной температуры, нагнетаемая ультратермостатом.

Динамометр демонстрируемого экземпляра прибора рассчитан на измерение усилий до 200 кг. 1 кг усилия вызывает в стеклянном измерителе разность хода $\sim 2{,}5$ ммк. Точность измерений разности хода достигает 0,01 ммк; точность измерения усилий при этом $\sim \pm 5$ г.

Примеры кривых сжатия и релаксации напряжений, полученных при помощи фотозаписи на микрофотометре МФ-4, приведены на рис. 2 и 3.

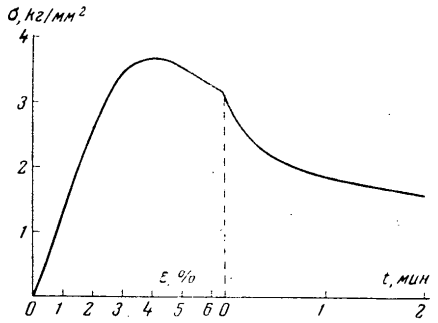

Рис. 2.

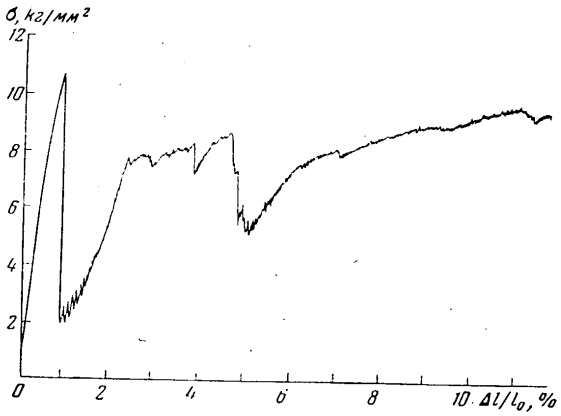

Рис. 3.

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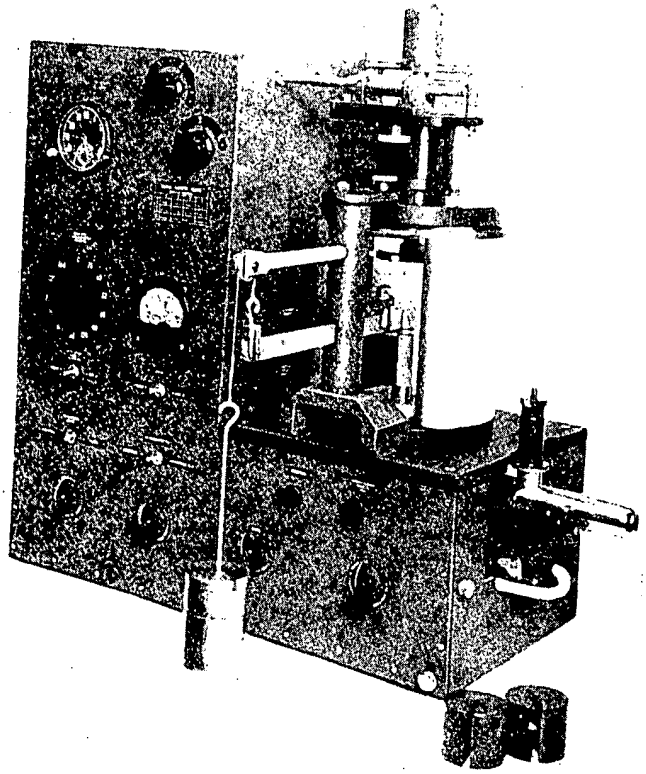

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N.V. Belov

Chapters A of The Crystal Chemistry of Silicates

Chapter A was based on the work done 30 years by W.L. Bragg and his collaborators and dealt chiefly with the silicates of Mg, Al and their metasomatic substituents, mainly in an either of the stages of oxidation. The salient feature of chapter A was the close fit (commensurability after V.Goldschmidt) between the edge of an Mg- or Al-octahedron and that of a Si-tetrahedron, which allows these silicates to have relatively simple crystal structures, most of which are based on the closest packing of O(OH,F)-atoms. Large cations, such as Na, Ca, La etc., K, were considered in this chapter only as filling voids, i.e. gaps between components which for this chapter were more important.

In chapter B where these large cations are predominant and play independent roles, they are themselves octahedrally co-ordinated. The edges of these large octahedra are incommensurable, i.e. not similar in length to those of the Si-tetrahedra, and the ordinary way in which silica enters the structures of chapter B is as the diorthogroup Si_2O_7. The vertical edges of a trigonal prism, in which the group Si_2O_7 can be inscribed, adjust themselves well (are similar in length) to the edges of the large (Ca, Na,...)-octahedra and in this way the diorthogroups Si_2O_7 play in chapter B the same role as the orthogroups SiO_4 possess in chapter A.

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The natural and synthetic Ca-hydrosilicates which are of importance in connection with cement provide the largest number of examples with isolated groups Si_2O_7 and have to illustrate the characteristic features of chapter B. Such compounds are the structures of cuspidine $Ca_4[Si_2O_7]F_2$, bilarite to $Ca_3[Si_2O_7][CO_3]_2$, tritomiteriliente xonotlite, or Ca = $Ca_6[Si_6O_{17}] \cdot (Ca(OH)_2)$. In all these structures the Ca-octahedra which are directly linked (through common edges) with the Si_2O_7-groups alternate with Ca-octahedra which have no direct links to Si_2O_7-groups This specific feature allows existence in these last octahedra of such cations as Zr, Mn and even Ti, all of which have ionic radii of intermediate size. A beautiful example is provided by the recently solved structure of the Na-Ca-Ti-silicate scyldesmite $Na_2Ca_2Ti_2Mn_2[Si_2O_7]_2O_2F_2$ in which every melanocratic cation is alternating with Na in a common column of octahedra. The groups Si_2O_7 are compressed between Na-octahedra. Scyldesmite and cuspidine now head two mineralogical groups of scyldesmite-rinkite and of cuspidine-wöhlerite, which one may call polymorphic as regards structures but not as regards individual compounds.

Silicate radicals analogous to the chains, double chains (or laths) of chapter A occur in chapter B, but instead of pyroxene chains with the formula $[Si_{1+1}O_3]_\infty$ we have pyroxenoid (wollastonite) chains with the formula

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$[Si_{2+1}O_9]_\infty$ and even $[Si_{3+1+1}O_{11}]_\infty$ (rhodonite). Then we come to doubled chains or laths as kind, instead of amphibole laths $[Si_6O_{17}]_\infty = [Si_{3+3}O_{11}]_\infty$ with hexagonal rings, a new type of monoclinic laths $[Si_6O_{17}]_\infty = [Si_{3+3}O_{11}]_\infty$ with octagonal rings. Such laths have recently been found not only in monetite but also in hillebrandite and perhaps are characteristic alps for foshagite.

One is led to conclusion that these octagonal rings are the most vital features of the hydrosilicates active in cement. At high temperatures (~ 790°) all such Ca-hydrosilicates lose their activity, being dehydrated to give parallel oriented fibres of inactive wollastonite.

When the chains and (amphibole) laths of chapter A condense to nets the only geometrically possible patterns is the well known one with hexagonal rings which occurs in talc, kaolin, micas and chlorites. But the same purely geometrical reasons do not permit the existence of nets with only octagonal rings. In chapter B octagonal rings must always alternate with tetragonal rings in the ratio 1:1 (apophyllite), with pentagonal rings in the ratio 1:2 (okenite), or with hexagonal and tetragonal rings in the ratio 3:1:1 (tobermorites). This last kind of net, the predominant details of which resemble those in monetite (with the monetite laths on two levels of this two-storied net), seems to be the most effective in giving cement properties.

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THE DIRECT CALCULATION OF STRUCTURE FACTORS FROM X-RAY DIFFRACTION DATA

РАСЧЕТ СТРУКТУРНЫХ АМПЛИТУД ПРЯМО ИЗ ДАННЫХ ПО ДИФФРАКЦИИ РЕНТГЕНОВСКИХ ЛУЧЕЙ

Many papers have recently dealt with the direct determination of phases or signs of structure factors from the distribution of the X-ray diffraction intensities in reciprocal lattice space. Direct methods of solving crystal structures include particularly methods of inequalities between structure factors (e. g. [1]) and statistical methods (e. g. [2]). Cochran [3] and the present author [4] proved that in some special cases certain structure factors, including their magnitudes and phases, can be calculated directly merely from the intensities of X-ray diffractions. It was shown that in principle both the magnitudes and the signs of structure factors with even indices can be calculated directly from diffraction data for centrosymmetrical crystal structures formed by the same kind of atoms according to the equation

$$U_{2H} = 2N|^{\circ}U_H|^2 - N^3|^{\circ}U_{K_i}|^2|^{\circ}U_{H-K_i}|^2 \qquad (1)$$

where $|^{\circ}U_H|^2 = |U_H|^2 - N^{-1}$ is the deviation of the square of the modulus of a unitary structure factor from its mean value; in the second term in the equation there is the mean value of the product $|^{\circ}U_{K_i}|^2 \cdot |^{\circ}U_{H-K_i}|^2$ for a sufficiently large number of K_i. The practical applicability of the equation is limited by the fact that the number of K_i must be such that the Patterson function calculated with the coefficients $|^{\circ}U_H|^2$ contains resolved spherically symmetrical peaks.

We arrive at the given equation for calculating U_{2H} as follows: If we have N identical atoms in the unit cell with coordinates $\pm r_j$, $j = 1, \ldots, \frac{1}{2}N$, then in the Patterson function of this structure after subtracting the main peak in the origin, there are N peaks corresponding to the interactions between the centrosymmetrical pairs of atoms, i. e. in the points $\pm 2r_j$, which have half the weight of $\frac{1}{2}(N^2 - 2N)$ maxima in the points $\pm (r_j \pm r_k)$, $j \neq k$, produced by other interactions.

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In the squared Patterson function the weights of these maxima in the first case are equal to unity and in the second to 4. If we subtract the square from the double of the Patterson function, there remain only the maxima in the points $\pm 2\boldsymbol{r}_j$ corresponding to the structure with double position vectors of the atoms. If we apply this consideration to the reciprocal space we obtain the above-mentioned relation between structure factors with even indices and intensities.

The magnitudes and phases of structure factors in more general cases can be calculated in a similar way. Let us deal in greater detail with the case of a structure without a centre of symmetry (P1), in the unit cell of which there are N atoms, $N-1$ of which are identical. The calculation can be easily carried out algebraically.

For the calculation a suitably normalized structure factor has the form

$$F_{\boldsymbol{H}} = p_0 + \sum_{j=1}^{N-1} e^{2\pi i \boldsymbol{H}\,.\,\boldsymbol{r}_j}, \tag{2}$$

where $p_0 = Z_0/Z_j$.

Since the origin of the unit cell in a crystal without a centre of symmetry can be chosen arbitrarily, we placed the origin in the position of the dissimilar atom. The square of the modulus of the structure factor can be suitably written as follows:

$$|F_{\boldsymbol{H}}|^2 = N - 1 + p_0^2 + 2p_0 \sum_{j=1}^{N-1} \cos 2\pi \boldsymbol{H}\,.\,\boldsymbol{r}_j + \sum_{\substack{j,\,k \\ j \neq k}}^{N-1} \cos 2\pi \boldsymbol{H}\,.\,(\boldsymbol{r}_j - \boldsymbol{r}_k) \tag{3}$$

The deviation of the square of the modulus of the structure factor from its mean value is

$$|^0F_{\boldsymbol{H}}|^2 = |F_{\boldsymbol{H}}|^2 - (N - 1 + p_0^2)\,.$$

The mean value of the products of these deviations is

$$\overline{|^0F_{\boldsymbol{K}_i}|^2 \,.\, |^0F_{\boldsymbol{H}-\boldsymbol{K}_i}|^2} = 2p_0^2 \sum_{j=1}^{N-1} \cos 2\pi \boldsymbol{H}\,.\,\boldsymbol{r}_j + \sum_{\substack{j,\,k \\ j \neq k}}^{N-1} \cos 2\pi \boldsymbol{H}\,.\,(\boldsymbol{r}_j - \boldsymbol{r}_k) \tag{4}$$

It can easily be seen that by subtracting (3) from (4) we get

$$\overline{|^0F_{\boldsymbol{K}_i}|^2 \,.\, |^0F_{\boldsymbol{H}-\boldsymbol{K}_i}|^2} - |^0F_{\boldsymbol{H}}|^2 = 2p_0(p_0 - 1)\,[^rF_{\boldsymbol{H}} - p_0] \tag{5}$$

where $^rF_{\boldsymbol{H}}$ is the real part of the structure factor and the quantities on the left side of the equation can be calculated from the intensities.

The Fourier series calculated with the real parts of the structure factors as coefficients gives us the structure together with its centrosymmetrical image.

Similar considerations led to results for crystals with a centre of symmetry.

We give here only the resultant equation for the case of a structure containing $N-2$ identical atoms in the unit cell with unknown positions and one pair of atoms different from these with known positions bound by the centre of symmetry ($P\bar{1}$).

With analogous normalization of the structure factors we obtain the equation

$$\begin{aligned} 2|^0F_{\boldsymbol{H}}|^2 - \overline{|^0F_{\boldsymbol{K}_i}|^2 \,.\, |F_{\boldsymbol{H}-\boldsymbol{K}_i}|^2} = 8p_0^2(p_0 - 1) - p_0(p_0^3 - 4p_0^2 + 2p_0 + 1)\cos 2\pi \boldsymbol{H}\,.\,\boldsymbol{r}_0 - \\ - 16p_0(p_0 - 1)\,F_{\boldsymbol{H}} \cos 2\pi \boldsymbol{H}\,.\,\boldsymbol{r}_0 + F_{2\boldsymbol{H}} \end{aligned} \tag{6}$$

The left side is known from the intensities and on the right side we know $|F_{\boldsymbol{H}}|$ and $|F_{2\boldsymbol{H}}|$ in addition to $\boldsymbol{r}_0$; their signs must be chosen so that the equation is satisfied. The applicability of Eqs. (5) and (6) is limited in the same way as that of Eq. (1).

Received 9. 1. 1958.

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A STATISTICAL METHOD FOR THE DETERMINATION OF THE SIGNS OF STRUCTURE FACTORS

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The average value of the products of a certain number of unitary structure factors was developed for a constant sum of their Miller indices. Its determination gives the measure of the usefulness of the statistical relations which connect the sign of a certain structure factor and the sign of the product of an arbitrary number of structure factors.

INTRODUCTION

One of the fundamental problems in crystal structure analysis is the determination of the phases of structure factors which, except for a multiplicative constant, are complex coefficients of the Fourier expansion for the real function of electron density in a crystal. From the intensities of reflections produced by the diffraction of X-rays by the space lattice of the crystal only the magnitude of the structure factors can be determined. To determine the phases some indirect methods are used. By combination of the diffraction data with the physical and chemical ones it is possible to find an approximate model of the structure which can be used to calculate structure factors and thus approximately determine their phases. The indirect methods most often used are those of trial and error [1] and the Patterson synthesis [2].

Methods, based on mathematical relations between the magnitudes of the structure factors corresponding to certain points of the reciprocal lattice, have recently been developed for the direct determination of the phases of the structure factors.

In 1948 Harker and Kasper [3] derived inequalities which limit the real part of some structure factors in terms of the magnitudes of others. The existence of inequalities among structure factors is based on the positivity of the electron density. To derive inequalities and to sharpen them it is convenient to introduce the so-called unitary structure factor

$$U_{\boldsymbol{H}} = \sum_{j=1}^{N} n_j e^{2\pi i \boldsymbol{H} \cdot \boldsymbol{r}_j} , \tag{1}$$

where n_j denotes that part of the total number of electrons in the unit cell corresponding to the j-th atom, the position vector of which is $\boldsymbol{r}_j$, $\boldsymbol{H}$ is the vector corresponding to a certain point in the reciprocal lattice, the sum is over all atoms of the unit cell. In [4] Hughes shows that inequality relations are limited in use when complicated structures with a large number of atoms have to be solved. Their applicability depends on the existence of at least some unitary structure factors with the value exceeding a certain minimum given by the type of inequality used. This minimum value decreases rapidly with an increasing number of atoms in the unit cell. Even when using the most powerful inequality relation deduced by Harker and Kasper for centrosymmetrical crystals [3]

$$|U_{\boldsymbol{H}} \pm U_{\boldsymbol{K}}|^2 \leqslant (1 \pm U_{\boldsymbol{H}+\boldsymbol{K}})(1 \pm U_{\boldsymbol{H}-\boldsymbol{K}}) , \tag{2}$$

at least 20% of the unitary structure factors must have a magnitude exceeding 0.30.

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Cochran [5] pointed out the probable equality of the signs of U_{H+K} and that of the product U_H and U_K for greater values of unitary structure factors, expressed by the relation

$$S_{H+K} = S_H \, . \, S_K \, , \tag{3}$$

where S_H is used to denote the sign of U_H. When the inequality (2) enables us to determine the signs of the structure factors, these signs are identical with those which follow from relation (3). Equation (3), however, holds for many cases when inequality (2) fails. The systematic use of this statistical method was worked out by Zachariasen [6] who proved the validity of the relation

$$S_H = S(\overline{S_{K_i} \, . \, S_{H-K_i}}) \, . \tag{4}$$

i. e. the sign of U_H is equal to the average sign of the products of the signs of the structure factors U_{K_i} and U_{H-K_i} for different K_i. Equation (4) is the statistical equivalent of equation (3). This relation was successfully used for the sign determination of structure factors of structures with a relatively large number of degrees of freedom, as for example in solving the crystal structure of metaboric acid [6].

For the average value of the products $U_H \, . \, U_K$ with $H + K$ constant and on the assumption that all atoms in the crystal are identical, Hughes [7] obtained

$$U_H \, . \, U_K \approx \frac{U_{H+K}}{N} \, , \tag{5}$$

where N is the number of atoms in the unit cell. Equation (5) gives the average value of the product $U_H \, . \, U_K$ including its sign which is identical with the sign of the chosen structure factor U_{H-K}. It may be assumed that in most cases the sign of the single products $U_H \, . \, U_K$ is equal to the sign U_{H-K}, at least for larger values of unitary structure factors.

Since the relations (3) and (4) are very useful for the sign determination of structure factors, the existence of similar relations for a greater number of combinations of structure factors is shown in the following section.

THE AVERAGE VALUE OF THE PRODUCTS OF STRUCTURE FACTORS

The expression for the unitary structure factor for a centrosymmetrical crystal with the origin of the unit cell placed in the centre of symmetry can be written as

$$U_H = 2 \sum_{j=1}^{N/2} n_j \cos 2\pi \boldsymbol{H} \, . \, \boldsymbol{r}_j \, . \tag{1}$$

For the product of m unitary structure factors we have

$$\prod_{k=1}^{m} U_{H_k} = 2^m \sum_{j_1}^{N/2} \sum_{j_2}^{N/2} \dots \sum_{j_m}^{N/2} \prod_{k=1}^{m} n_{j_k} \cos 2\pi \, \boldsymbol{H}_k \, . \, \boldsymbol{r}_{j_k} \, . \tag{6}$$

The righthand side of expression (6) can be written by means of a formula which expresses the products of cosines of different arguments by the summation formula of cosines. By the method of mathematical induction the relation

$$2^m \prod_{k=1}^{m} \cos \alpha_k = \sum_{l=0}^{m} \left\{ \sum_{i_l=1}^{\binom{m}{l}} \cos \left[\sum_{k=1}^{m} \operatorname{sign} (k_{i_l}) \, \alpha_k \right] \right\} , \tag{7}$$

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was proved, where l denotes the number of negative signs of α_k and sign (k_{i_l}) denotes the sign of α_k in the argument of the cosine in the i_l-th combination of l negative and $m - l$ positive signs of α_k.

By means of relation (7) equation (6) can be written in the form

$$\prod_{k=1}^{m} U_{\boldsymbol{H}_k} \sum_{j_1}^{N} \sum_{j_2}^{N/2} \cdots \sum_{j_m}^{N/2} \prod_{k=1}^{m} n_{j_k} \left[\sum_{l=0}^{m} \left\{ \sum_{i_l=1}^{\binom{m}{l}} \cos 2\pi \left[\sum_{k=1}^{m} \operatorname{sign}(k_{i_l})\, \boldsymbol{H}_k \,.\, \boldsymbol{r}_{j_k} \right] \right\} \right]. \quad (8)$$

By separating the terms for which $j_1 = j_2 = \ldots = j_m$ we obtain

$$\prod_{k=1}^{m} U_{\boldsymbol{H}_k} \cdots \sum_{j}^{N/2} n_j^m \sum_{l=0}^{m} \left\{ \sum_{i_l=1}^{\binom{m}{l}} \cos 2\pi \left[\sum_{k=1}^{m} \operatorname{sign}(k_{i_l})\, \boldsymbol{H}_k \right] . \boldsymbol{r}_j \right\} +$$

$$\sum_{j_1}^{N/2} \sum_{j_2}^{N/2\,\prime} \cdots \sum_{j_m}^{N/2\,\prime} \prod_{k=1}^{m} n_{j_k} \left[\sum_{l=0}^{m} \left\{ \sum_{i_l=1}^{\binom{m}{l}} \cos 2\pi \left[\sum_{k=1}^{m} \operatorname{sign}(k_{i_l})\, \boldsymbol{H}_k \,.\, \boldsymbol{r}_{j_k} \right] \right\} \right], \quad (8')$$

where the symbol Σ' denotes summation for such indices $j_1, j_2, \ldots, j_m$ at least two of which are different.

By determining the averages of the products of structure factors the indices of which are chosen so that $\sum_{k=1}^{m} \operatorname{sign}(k_{i_l})\, \boldsymbol{H}_k$ is constant, i. e. for a definite combination of signs at $\boldsymbol{H}_k$ in the argument of the cosine, only that term in (8′) for which the given sum is constant will have an average value different from zero. The other terms will average zero because their values and signs in different products are different for the same sign combination at $\boldsymbol{H}_k$ so that the average value of products of m structure factors chosen in this way will be

$$\prod_{k=1}^{m} U_{\boldsymbol{H}_k}^{\sum_{k=1}^{m} \operatorname{sign}(k_{i_l})\, \boldsymbol{H}_k} \sum_{j}^{N} n_j^m \cos 2\pi \left[\sum_{k=1}^{m} \operatorname{sign}(k_{i_l})\, \boldsymbol{H}_k \right] . \boldsymbol{r}_j \,. \quad (9)$$

A statistical sign relation is obtained from the average value of the products of structure factors thus determined. Thus, for example, if

$$\sum_{k=1}^{m} \operatorname{sign}(k_{i_l})\, \boldsymbol{H}_k = 0 \,, \quad (10)$$

(9) will take the form

$$\overline{\prod_{k=1}^{m} U_{\boldsymbol{H}_k}}^{0} = \sum_{j}^{N} n_j^m \,, \quad (11)$$

which means that the average of the products of U_k chosen according to (10) must be positive. It can be deduced from this that at least the large values of the products considered in taking averages are positive, for otherwise the resulting average value would be more likely negative. If, for example, the signs of $m - l$ structure factors are known and thus also the sign of their product, then the m-th structure factor, satisfying condition (10), will probably have the same sign. This probability will be greater, the larger the value of this product and the m-th structure factor.

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Relation (11) holds for crystals with a centre of symmetry independent of the kind of atoms in the crystal. If the crystal is composed of equal atoms, i. e. $n_j = 1/N$, then equation (9) can be written

$$\prod_{k=1}^{m} U_{\mathbf{H}_k}^{\sum_{k=1}^{m} \operatorname{sign}(k_{i_l})\,\mathbf{H}_k} = N^{1-m} U_{\sum_{k=1}^{m} \operatorname{sign}(k_{i_l})\,\mathbf{H}_k} \qquad (12)$$

DISCUSSION AND PRACTICAL APPLICATION

It can be seen from (11) that the probability that the m-th unitary structure factor has the same sign as the product of the $m - l$ structure factors is greater the larger the value of the sum on the righthand side of equation (11). This value depends on N, n_j and m.

With an increasing number of atoms in the unit cell of the crystal, i. e. with increasing N, the average values of n_j will decrease and thus for a certain $m > 1$ the value of the sum in (11) will also decrease.

For a crystal composed of unequal atoms, i. e. for different n_j, the righthand side of (11) will be greater for the same N than for a crystal formed of the same number of equal atoms.

Finally, it can be seen that the average value of the product of m unitary structure factors decreases with increasing m. The form of (11) for several values of m is given as an example:

a) $m = 1$: in this case (11) reduces to

$$U_0 = 1\,, \qquad (13)$$

since $\sum_j n_j = 1$, and gives a trivial result.

b) $m = 2$: for this value of m (11) has the form

$$\overline{U_{\mathbf{H}_1}^2} = \sum_j^N n_j^2 \qquad (14)$$

and leads to the known result for the average value of the square of the modul of the unitary structure factor.

c) $m = 3$: only for this value of m do we obtain a statistical relation which can be used for the sign determination

$$\overline{U_{\mathbf{H}_1} \cdot U_{\mathbf{H}_2} \cdot U_{\mathbf{H}_3}}^0 = \sum_j^N n_j^3\,. \qquad (15)$$

Cochran's statistical relation (3) follows from (15) for larger values of unitary structure factors. For the derivation of this relation Cochran used the Sayre [8] equation which strictly holds only for crystals formed of identical atoms and thus proved it only for atoms of the same type. In [7] Hughes showed the validity of Cochran's relation for a crystal with equal atoms on the basis of the above equation (5). From (15) it is obvious that relation (3) holds better for crystals composed of unequal atoms.

d) $m = 4$: for this m (11) gives

$$\overline{U_{\mathbf{H}_1} \cdot U_{\mathbf{H}_2} \cdot U_{\mathbf{H}_3} \cdot U_{\mathbf{H}_4}}^0 = \sum_j^N n_j^4\,. \qquad (16)$$

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Similar relations can also be obtained for $m > 4$. They cannot be used in practice for limiting the choice of signs of structure factors because of the tendency of the sum on the righthand side of (11) to decrease with increasing m.

Equation (12) can also be used for crystals composed of equal atoms. Its special form for $m = 2$ is identical with Hughes' equation (5) which again resembles Cochran's relation (3). From $m = 3$ we obtain from (12) the relation

$$\overline{U_{\boldsymbol{H}_1} \cdot U_{\boldsymbol{H}_2} \cdot U_{\boldsymbol{H}_3}^{-\boldsymbol{H}_1+\boldsymbol{H}_2+\boldsymbol{H}_3}} = \frac{1}{N^2} U_{\boldsymbol{H}_1+\boldsymbol{H}_2-\boldsymbol{H}_3} . \tag{17}$$

For $\boldsymbol{H}_1 + \boldsymbol{H}_2 + \boldsymbol{H}_3 = 0$ we have from (17)

$$\overline{U_{\boldsymbol{H}_1} \cdot U_{\boldsymbol{H}_2} \cdot U_{\boldsymbol{H}_3}^{0}} = \frac{1}{N^2} , \tag{18}$$

or $U_0 = 1$. From this relation (3) again follows. Relation (18) is very useful because its righthand side has its maximum possible value since $(U_{\boldsymbol{H}_1+\boldsymbol{H}_2+\boldsymbol{H}_3}) \leq U_0$.

Most useful statistical relations result by choosing large unitary structure factors for $U_{\boldsymbol{H}_1+\boldsymbol{H}_2-\boldsymbol{H}_3}$. If for example $|U_{\boldsymbol{H}_1+\boldsymbol{H}_2-\boldsymbol{H}_3}| = 0.50$ then (17) gives for the probability, that the sign of the product $U_{\boldsymbol{H}_1} \cdot U_{\boldsymbol{H}_2} \cdot U_{\boldsymbol{H}_3}$ is the same as that of $U_{\boldsymbol{H}_1+\boldsymbol{H}_2-\boldsymbol{H}_3}$, one half of that value which follows from relation (18). The sign relationship (3) gives without doubt more correct signs than by applying (17), but by choosing for $U_{\boldsymbol{H}_1+\boldsymbol{H}_2-\boldsymbol{H}_3}$ in (17) a set of large unitary structure factors more statistical combinations are obtained than from Cochran's relationships. It is obvious that every large unitary structure factor gives us an equivalent set of relations as by applying (3) which limits itself with $\boldsymbol{H}_1 + \boldsymbol{H}_2 + \boldsymbol{H}_3 = 0$.

The reliability and usefulness of (17) for $\boldsymbol{H}_1 + \boldsymbol{H}_2 + \boldsymbol{H}_3 \neq 0$ were demonstrated on the known structure of β-selenium [9]. The method was used to determine the signs of structure factors of the $h0l$ zone. $U_{607} = +0.66$ was chosen as the $U_{\boldsymbol{H}_1+\boldsymbol{H}_2+\boldsymbol{H}}$ and the statistical relations were carried out for 50 independent unitary structure factors with an absolute value greater than 0.18. In this way 98 independent products were obtained.

Table I shows the results obtained.

Table I.

	No. of valid relations	No. of non-valid relations
0.20 — 0.25	19	14
0.25 — 0.30	43	9
0.30 — 0.35	40	5
0.35 — 0.40	28	1
0.40 — 0.45	7	1
0.45 — 0.50	1	0

Table I gives the number of the correct and incorrect indications for the product of three unitary structure factors according to relation (17), the root-mean-square values of which lie in the intervals, given in the first column.

When postulating $\boldsymbol{H}_1 + \boldsymbol{H}_2 + \boldsymbol{H}_3 = \text{const.}$ by application (16) for crystals composed of unequal atoms only a limited number of products of structure

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factors required by equation (16) are obtained. If we suppose the average value of this limited number of products of structure factors to be positive, at least for large $|U_{\boldsymbol{H}_1+\boldsymbol{H}_2+\boldsymbol{H}_3}|$, which again resembles (16), by choosing $\boldsymbol{H}_1 + \boldsymbol{H}_2 + \boldsymbol{H}_3 = \text{const.}$ suitable statistical relations can be formed. This case was followed on the known structure of metaboric acid [6]. The statistical relations were proved for the product of the structure factors of the $h0l$ zone. The number of independent U_{h0l} was 22 with an absolute value greater than 0.26 and $U_{408} = +\ 0.56$ was chosen for $U_{\boldsymbol{H}_1+\boldsymbol{H}_2+\boldsymbol{H}_3}$. Table 2 shows the results obtained for 40 independent products.

Table 2.

	No. of valid relations	No. of non-valid relations
0.20 — 0.30	12	2
0.30 — 0.40	15	1
0.40 — 0.50	9	0
0.50 — 0.55	1	0

The above examples indicate the statistical reliability of the theoretical considerations given in the preceding chapter. As expected, the statistical relations hold better for products with sufficiently large unitary structure factors.

The author wishes to thank M. Týcová for carefully carrying out the calculations in the practical applications.

Received 15. 12. 1954.

СТАТИСТИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ ЗНАКОВ СТРУКТУРНЫХ АМПЛИТУД

(Содержание предыдущей статьи)

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В настоящей работе дополнены статистические методы определения знаков структурных амплитуд. Выводится среднее значение произведений произвольного числа единичных амплитуд в случае, если сумма принадлежащих им индексов Миллера постоянна. Произведение m единичных структурных амплитуд для центросимметрических кристаллов можно с помощью уравнения (1) написать в виде (6). Используя (7), где l показывает число отрицательных знаков α_k и sign (k_{il}) обозначает знак α_k в аргументе косинуса i_l-той комбинации l отрицательных и $m - l$ положительных знаков α_k выражение (6) можно написать в виде (8). Выделяя члены, для которых $j_1 = j_2 = \ldots = j_m$, и обозначая Σ' суммы, просуммированные по таким индексам $j_1, \ldots, j_m$, из которых по крайней мере два различны, мы получим (8). Среднее значение произведений m структурных амплитуд с индексами, выбранными таким образом, чтобы сумма $\sum_{k=1}^{m} \text{sign}\,(k_{il})\,\boldsymbol{H}_k$ была постоянной, тогда дано выражением (9).

На основании среднего значения, определенного таким образом, можно получить статистическое соотношение между знаками структурных амплитуд. Выбирая произведение $\boldsymbol{H}_k$ согласно (10), мы получим из (9) соотношение (11). Это соотношение имеет место для

Approved For Release 2009/04/16 : CIA-RDP80T00246A007000350002-4

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кристаллов, образованных из неодинаковых атомов, для атомов среднего сорта $n_j = 1/N$, и мы получим выражение (12).

В последней главе обсуждаются полученные соотношения. Из (11) видно, что вероятность ожидать, что m-тая единичная структурная амплитуда имеет тот же знак, что и произведение $m - 1$ амплитуд, тем больше, чем больше величина суммы в правой стороне уравнения (11). Поэтому исследуется ее зависимость от N, n_j и m. Для $m = 1, \ldots$ $m = 4$ мы получим соотношения (13), (14), (15), и (16).

Для атомов одного и того же сорта и для $m = 3$ уравнение (12) принимает форму (17). При выборе $\mathbf{H}_1 + \mathbf{H}_2 + \mathbf{H}_3 = 0$ мы получим соотношение (18); это известное соотношение Кокрена. Применением уравнения (17) мы можем привести структурные амплитуды к удобному статистическому соотношению так, что выберем $U_{\mathbf{H}_1 \cdot \mathbf{H}_2 + \mathbf{H}_3}$ равным какой-нибудь единичной структурной амплитуде с достаточно большим абсолютным значением. Несмотря на то, что область применения соотношения Кокрена больше, можно таким образом получить гораздо больше статистических комбинаций, так как для любой большие единичной структурной амплитуды мы получим эквивалентное число соотношений как и при методе Кокрена. Применимость соотношения (17) при выборе $\mathbf{H}_1 + \mathbf{H}_2 + \mathbf{H}_3 \neq 0$ была проверена на известной структуре β-селена, соотношение (16) проверялось на структуре метаборной кислоты. Результаты статистик приведены в таблицах № 1 и 2.

Поступило 15. 12. 1954.

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Approved For Release 2009/04/16 : CIA-RDP80T00246A007000350002-4